Analysis of Airborne Molecular Contaminants (AMC) in the cleanroom for the semiconductor industry

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Generality : NIOSH & OSHA

In the Unites States, the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) offer, for many such substances, specific recommendations on collecting (trapping) the contaminant.

Merck SA procedures are performed according to the NIOSH and OSHA methodologies.
In response to this need, SEMI issued SEMI F21-95 standard, “Classification of Airborne Molecular Contaminant levels in Clean Environments”, to classify clean environments with respect to 4 classes of molecular contaminants, including:

- Molecular Acids (MA)
- Molecular Bases (MB)
- Molecular Condensables (MC)
- Molecular Dopants (MD)
**AMC related Process issues**

<table>
<thead>
<tr>
<th>Acids &amp; Bases</th>
<th>Condensables</th>
<th>Dopants</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>□ Fab Corrosion</td>
<td>□ Adhesion Failures</td>
<td>□ Uncontrolled B, P doping</td>
<td>□ Degradation of electrical properties of Si substrate (E.g.: Carrier lifetime, Leakage currents)</td>
</tr>
<tr>
<td>□ Etch rate Shifts</td>
<td>□ SiC formation (after preoxidation clean)</td>
<td>□ Threshold Voltage Shifts</td>
<td>□ High contact resistance</td>
</tr>
<tr>
<td>□ DUV Photoresist T-topping</td>
<td>□ High contact resistance</td>
<td>□ Resistivity Shifts</td>
<td>□ Gate oxide integrity</td>
</tr>
<tr>
<td>□ Wafer and Optics Hazing</td>
<td>□ Gate oxide integrity</td>
<td>□ Nucleation irregularities</td>
<td>□ HEPA filter degradation or outgassing of B &amp; P</td>
</tr>
<tr>
<td>□ Metallization Corrosion</td>
<td>□ Ineffective cleaning</td>
<td>□ HEPA filter degradation or outgassing of B &amp; P</td>
<td>□ Threshold voltage shifts</td>
</tr>
</tbody>
</table>
Sampling Methodology: 2 possibilities!!!

- **Airborne Sampling**: Sampling of cleanroom air is conducted over an 8-24 hours period using sampling systems that have proven efficient for capturing acids, bases, dopants, salts, trace metals, and organics.

- **Witness Wafer**: Contaminants of cleanroom air are collected by a witness wafer exposed for about 7 days period for capturing acids, bases, dopants, salts, and trace metals.
Sampling Pump System

Choice of the sampling pump system:

**SUPELCO Q - Max pump**

- Connection
- Indicator
- Control
Sampling Pump Characteristic

Choice of the sampling pump system:

- Flow regulation from 0.5 to 3 L/mn.
- Time meter.
- Recalibration every 200 hours.
- Compensation of the pressure.
- If flow interrupted for 1.5 mn, break in the pumping and in the time adding meter.
- 220 V Mains or Electric battery (autonomy = 11.5 h.).
Particular Metals Monitoring
(NIOSH 7300)

1. Witness Wafers 8":
   - Time of Exposure = 7 days
   - VPD ICP-MS analyses
   - QL < $10^9 - 10^{10}$ At/cm² depends on the element

2. Airborne Sampling:
   - Time = 8 - 24 hours
   - Cassette + Filter
   - ICP-OES Analysis
   - Limit < 1 µg/m³
1. Witness Wafers 8" :

- Time of Exposure = 7 days
- ILC Analysis (Dionex DX 500)
- QL : Anions/cm², depends on the element

\[ \text{QL (E}^{12}\text{ Anions/cm}^2) \]

<table>
<thead>
<tr>
<th>Elements</th>
<th>Chloride</th>
<th>Fluoride</th>
<th>Nitrate</th>
<th>Nitrite</th>
<th>Bromide</th>
<th>Sulfate</th>
<th>Phosphate</th>
<th>Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{QL} )</td>
<td>1,7</td>
<td>6,3</td>
<td>1,9</td>
<td>2,6</td>
<td>2,2</td>
<td>2,5</td>
<td>2,5</td>
<td>210</td>
</tr>
</tbody>
</table>
2. Airborne sampling:

- Time = Either 8 hours or 24 hours
- Impinger for eluent NaHCO$_3$ / Na$_2$CO$_3$
- ILC Analysis (DX 500 / DX 120)
- QL : < 1µg/m$^3$

Cl$^-$ / F$^-$ / NO$_3^-$ / NO$_2^-$ / Br$^-$ / SO$_4^{2-}$
/ PO$_4^{3-}$ / CH$_3$COO$^-$
1. Witness Wafers 8"
   - Time of exposure = 7 days
   - Liquid extraction & ILC Analysis (Dionex DX 500)
   - QL < $1.3 \times 10^{13}$ Ion/cm$^2$

2. Airborne Sampling
   - Time = 24 hours
   - Impinger eluent sulfonic Acid
   - ILC Analysis (Dionex DX 500)
   - QL : < 1 µg/m$^3$

Ammonium Total $\text{NH}_4^+$
Specific Condensables Monitoring

Benzen - Toluen - Xylen – Ethyl Benzen
- IPA – Ethyl Lactate - HMDS - PGMEA - Cyclohexanon - Anisole - MEK

Airborne Sampling:

- Time = Either 3 hours
- Desorption selective tubes
- ATD - GC -FID (Perkin Elmer)
- Unit: < µg/m³
### Performance : Limit of quantification

<table>
<thead>
<tr>
<th>Elements</th>
<th>QL* (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzen</td>
<td>&lt; 0.7</td>
</tr>
<tr>
<td>Toluen</td>
<td>&lt; 1.2</td>
</tr>
<tr>
<td>P-Xylen</td>
<td>&lt; 1.1</td>
</tr>
<tr>
<td>Ethyl Benzen</td>
<td>&lt; 1.2</td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Ethyl Lactate</td>
<td>Improvement</td>
</tr>
<tr>
<td>HMDS</td>
<td>&lt; 10.2</td>
</tr>
<tr>
<td>PGMEA</td>
<td>Improvement</td>
</tr>
<tr>
<td>Cyclohexanon</td>
<td>&lt; 3.2</td>
</tr>
<tr>
<td>Anisole</td>
<td>&lt; 1.1</td>
</tr>
<tr>
<td>Mehtyl Ethyl Keton</td>
<td>&lt; 4.5</td>
</tr>
</tbody>
</table>

* : calculated with 1 Liter of air
Total Condensables Monitoring
(NIOSH 2549)

Gas Chromatography - MS
+ Thermal desorption
Dopants Monitoring

Boron & Phosphorus

1. Witness Wafers 8" :
   - Time of exposure = 7 days
   - Liquid extraction & ILC Analysis (Dionex DX 500)
   - $Q_L_{\text{Boron}} < 6.9 \times 10^{12} \text{ At/cm}^2$
   - $Q_L_{\text{Phosphorus}} < 8.9 \times 10^{11} \text{ At/cm}^2$

2. Airborne Sampling (Particular B & P contaminants) :
   - Time = 24 hours
   - Cassette + Filter
   - ICP-OES Analysis
   - Limit < 1 $\mu$g/m$^3$
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